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- (54) Curable polymer composition comprising organic polymer having silicon-containing reactive group.

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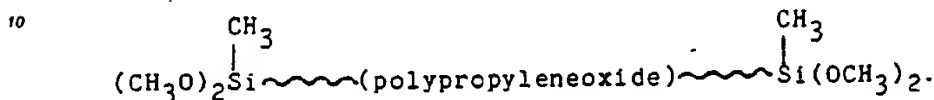
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Description

The present invention relates to a curable polymer composition comprising an organic polymer having at least one silicon-containing reactive group in a molecule, which composition is readily cured.

- 5 An organic polymer having at least one silicon-containing reactive group is known in the field. This polymer is similar to moisture curable polysiloxane in that it cures by forming siloxane linkage, but is different in that it contains an organic polymer in the backbone chain. One example of such polymer is a polymer of the formula:



- 15 This polymer can cure by forming siloxane linkage in the presence of moisture.

The organic polymer having at least one silicon-containing reactive group can be used as a pressure sensitive adhesive and a sealant (cf. U.S. Patent Nos. 4,463,115 and 3,971,751).

- 20 Usually, a curing catalyst is used for curing the organic polymer having at least one silicon-containing reactive group. As the curing catalyst, there are known various compounds such as titanate esters (e.g. tetra-n-butoxytitanate), tin carboxylate compounds (e.g. dibutyltin dilaurate and tin dioctylate) and amines. Although these catalysts are selected and used according to the final use and application of the curable composition, generally they have low catalytic activity and only provide a low curing rate. Therefore, a highly active curing catalyst which can cure the composition at a high rate is desired.

- 25 In the case where the polymer is used as the pressure sensitive adhesive, the polymer is required to cure in a very short period of time, i.e., within one minute, for effective production of the adhesive. Among the curing catalysts described above, titanate esters and a combination of tin carboxylate and amine have fairly high curing activity. However, the pressure sensitive adhesive containing titanate ester has drawbacks such as discoloring of the adhesive. The pressure sensitive adhesive containing tin carboxylate and amine has drawbacks such as discoloring and odor due to amine, and bleeding of amine on the surface of the pressure sensitive adhesive which results in change of adhesive properties.

- 30 In the case where the polymer is used as the sealant, the curing catalyst having high activity is required for shorter term of works. The sealant composition containing tin carboxylate and amine has high curing rate, but has low adhesivity to a substrate which is one of the important properties of the sealant. Moreover, the sealant composition containing tin carboxylate has such a drawback that the activity of the catalyst is decreased after the storage of the composition.

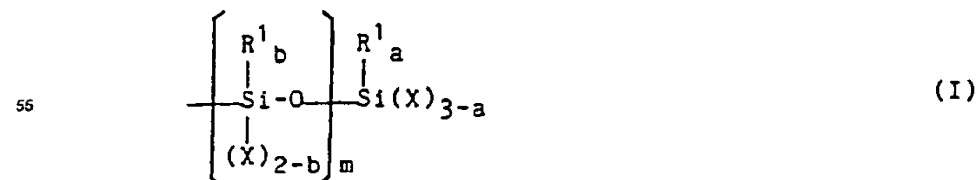
35 An object of the present invention is to provide a curable polymer composition comprising an organic polymer having at least one silicon-containing group in a molecule and a curing catalyst which can cure the polymer at a high curing rate.

- 40 Another object of the present invention is to provide a curable polymer composition having a high curing rate which is suitable for a pressure sensitive adhesive.

Further object of the present invention is to provide a curable polymer composition having a high curing rate even after long term storage.

Still another object of the present invention is to provide a curable polymer composition having a high curing rate and high adhesivity to a substrate.

- 45 Accordingly, the present invention relates to a curable polymer composition comprising
(A) 100 parts by weight of an organic polymer comprising a backbone chain selected from polyalkyleneoxide with a molecular weight of 500 to 30,000, ether-ester block copolymer, vinyl polymer, vinyl type polymer with a molecular weight of 500 to 1,000,000 and diene type polymer and having at least one silicon-containing reactive group of the formula (I)

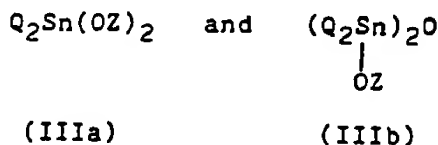


wherein R¹ is, the same or different, a C₁-C₂₀ monovalent hydrocarbon group or a triorganosiloxy group of the formula:



in which R¹ is, the same or different, a C₁-C₂₀ monovalent hydrocarbon group; X is a hydroxyl group or a hydrolyzable group provided that when the number of Xs in the group (I) is at least 2, Xs are the same or different; a is 0, 1, 2 or 3; b is 0, 1 or 2; and m is an integer of 1 to 18; wherein the silicon-containing reactive group (I) is bonded to the backbone chain via a carbon atom directly attached to the silicon atom, and

(B) 0.01 to 10 parts by weight of a curing catalyst selected from the compounds of the formulas:



wherein Q is a C₁-C₂₀ monovalent hydrocarbon group; and Z is, the same or different, a C₁-C₂₀ monovalent hydrocarbon group or an organic group having a functional residue which can form a coordinate bond with Sn atom.

The silicon-containing reactive group (I) can initiate a condensation reaction in the presence of a catalyst and optionally in the presence of water or moisture or a cross-linking agent.

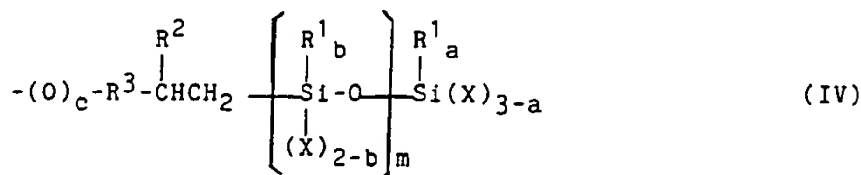
When at least two R¹ groups are present in the group (I), they may be the same or different. Specific examples of the hydrocarbon group of R¹ are an alkyl group (e.g. methyl, ethyl), a cycloalkyl group (e.g. cyclohexyl), an aryl group (e.g. phenyl) and an aralkyl group (e.g. benzyl). R¹ may be a triorganosiloxy group (II). Among them, methyl and phenyl are preferred.

Specific examples of the hydrolyzable group of X are halogen, hydride, alkoxy, acyloxy, ketoxymate, amino, amide, aminoxy, mercapto and alkenyloxy. Among them, alkoxy is preferred.

The silicon-containing group (I) preferably has at least one X, more preferably 1 to 4 Xs.

The organic polymer (A) should have at least one silicon-containing reactive group (I) per molecule, and preferably 1.2 to 6 reactive groups per molecule on the average.

The silicon-containing reactive group (I) chemically bonds to the backbone chain of the organic polymer via a carbon atom directly attached to the is not desirable for the silicon-containing reactive group to be bonded to the backbone chain through a bonding structure of the formula: =Si-O-C=, since such structure tends to be cleaved by water. The bonding structure between the silicon atom of the reactive group and the backbone chain or its side chain can be expressed by a structure of the formula: =Si-C=. Preferably, the reactive group is bonded to the backbone chain in the following chemical structure:



wherein R¹, X, a, b and m are the same as defined above. R² is a hydrogen atom or a C₁-C₂₀ monovalent organic group; R³ is a C₁-C₂₀ divalent organic group; and c is 0 or 1.

When the alkyleneoxide polymer constitutes the backbone chain polymer of the organic polymer (A), it preferably comprises repeating units of the formula:

-R⁴-O-

wherein R⁴ is a C₁-C₈, preferably C₁-C₄ divalent hydrocarbon group. Specific examples of the divalent group R⁴ are those of the formulas:

-CH₂-, -CH₂CH₂-, -CH(CH₃)CH₂-, -CH(C₂H₅)CH₂-, -C(CH₃)₂CH₂- and -CH₂CH₂CH₂CH₂-. Among them,

-CH(CH₃)CH₂- is preferred.

The backbone chain of the alkyleneoxide polymer may comprise one or more kinds of repeating units.

The alkylene oxide polymer has a molecular weight of 500 to 30,000, preferably 3,000 to 15,000. Particularly, one having a silicon-containing reactive group at the end of molecule and a molecular weight of 3,000 to 15,000 is desirable.

As the backbone chain of the organic polymer (A), an elastic polymer comprising a vinyl compound and/or a diene compound can be used. Specific examples of such polymer are polybutadiene, styrene/butadiene copolymer, acrylonitrile/butadiene copolymer, acrylate/butadiene copolymer, ethylene/butadiene copolymer, vinylpyridine/butadiene copolymer, ethylene/propylene copolymer, ethylene/vinyl acetate copolymer, ethylene/acrylate copolymer, polyisoprene, styrene/isoprene copolymer, isobutylene/isoprene copolymer, polychloroprene, styrene/chloroprene copolymer, acrylonitrile/chloroprene copolymer, polyisobutylene, polyacrylate and polymethacrylate. Among them, the organic polymer (A) comprises at least 50 % by weight of acrylate or methacrylate (hereinafter referred to as "(meth)acrylate") is preferred. Preferred (meth)acrylate is ester of (meth)acrylic acid with a straight or branched C₂-C₁₂ alkyl or cycloalkyl alcohol. Specific examples of (meth)acrylate are n-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isobutyl (meth)acrylate, amyl (meth)acrylate, hexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-octyl (meth)acrylate and n-decyl (meth)acrylate.

The vinyl type polymer has a molecular weight of 500 to 1,000,000, preferably 2,000 to 500,000. Particularly, one having a molecular weight of 3,000 to 15,000 is preferred when the silicon-containing group is present as a terminal group.

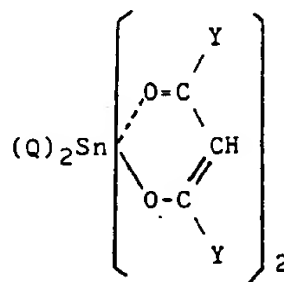
The organic polymer (A) may be used alone or as a mixture with at least one other organic polymer (A). For example, a mixture of the alkyleneoxide polymer and the vinyl type polymer such as polyalkyl acrylate can be used. Further, a polymer prepared by polymerizing the vinyl compound such as alkyl acrylate in the presence of the alkyleneoxide polymer can be used.

The organic polymer (A) having a backbone chain comprising the alkyleneoxide polymer or the ether-ester block copolymer may be prepared by one of the methods described in U.S. Patent Nos. 3,592,795 and 3,408,321, Japanese Patent Publication No. 32673/1974, Japanese Patent Kokai Publication Nos. 156599/1975, 73561/1976, 6096/1979, 13768/1980, 82123/1980, 123620/1980, 125121/1980, 131021/1980, 131022/1980, 135135/1980 and 137129/1980.

The organic polymer (A) having a backbone chain comprising the vinyl type polymer or copolymer may be prepared by one of the method described in U.S. Patent No. 3,453,230, Japanese Patent Publication No. 28301/1976 and Japanese Patent Kokai Publication No. 179210/1982.

The organic polymer (A) having a backbone chain comprising the diene type polymer may be prepared by one of the method described in Japanese Patent Publication No. 17553/1970 and Japanese Patent Kokai Publication No. 1839/1972.

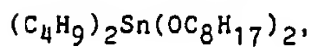
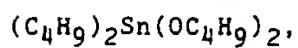
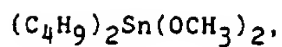
The curing catalyst (IIIa) or (IIIb) to be used according to the present invention initiates the condensation reaction of the silicon-containing reactive groups of the organic polymer (A) in the presence or absence of water or moisture to cure the polymer (A). The catalyst (IIIa) in which Z is the organic group having the functional residue which can form the coordinate bond with Sn atom can be used. An example of such catalyst is a compound represented by the formula:



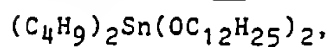
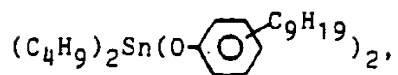
wherein Q is, the same or different, a C₁-C₂₀ monovalent hydrocarbon group; and Y is, the same or different, a C₁-C₈ hydrocarbon group, halogenated hydrocarbon group, cyanoalkyl group, alkoxy group, halogenated alkoxy group, cyanoalkoxy group or amino group.

Specific examples of the curing catalyst are those of the formulas:

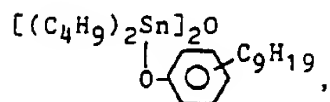
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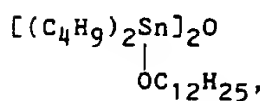
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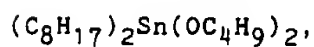
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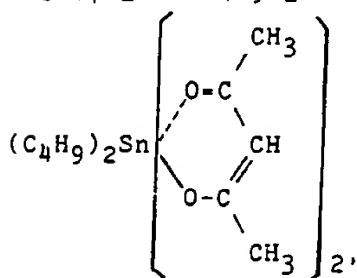
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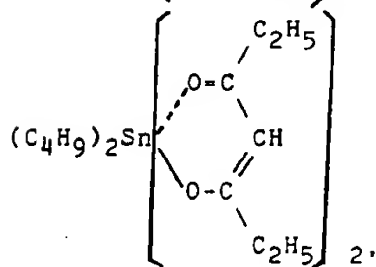
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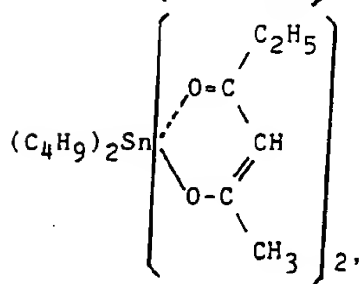
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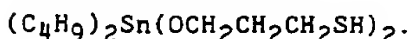
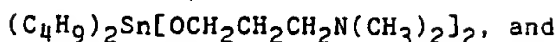
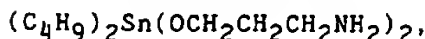
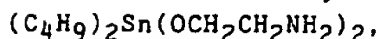
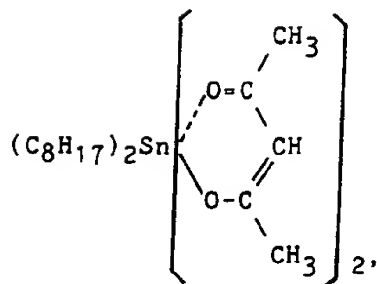


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The catalyst (B) may be used alone or mixture with at least one of other catalysts (B). The amount of the catalyst to be used is 0.01 to 10 parts by weight per 100 parts by weight of the organic polymer (A).

The curing catalyst used according to the present invention has higher curing activity than the conventionally used organotin compound. Moreover, the curing catalyst used according to the present invention does not discolor the cured polymer.

The composition of the invention finds various application including a pressure sensitive adhesive composition and a sealing material.

When the composition of the invention is used as the pressure sensitive adhesive, it is applied on a tape, sheet, label or foil. Namely, the composition in the form of a non-solvent type liquid, a solution, an emulsion or a hot melt type may be applied on a substrate such as a film of a synthetic or modified natural resin, paper, fabrics, metal foil, metallized plastic foil, asbestos or glass fiber fabrics and cured at a room temperature or an elevated temperature with optional exposure to water or moisture.

To regulate the adhesion characteristics of the composition, a tackifier resin may be added to the composition. Specific examples of the tackifier resin are resins having a polar group such as rosin ester resin, phenol resin, xylene resin, xylene-phenol resin, terpene-phenol resin; petroleum resins with relatively small polarity such as aromatic polymer, aliphatic-aromatic copolymer and alicyclic polymer; cumaron resin; low molecular weight polystyrene; terpene resin. Commercially available tackifier resins are as follows:

Resins with comparatively small polarity:

Petrosin 80®, Tackaoe A 100® and FTR 6100® (Mitsui Petrochemical Industries Co., Ltd., Japan), Neopolymer S® (Nippon Petrochemical Co., Ltd., Japan), Quinton 1500® (Nippon Zeon Co., Ltd. Japan), Picolasteck A 75® (Hercules Inc.), and Cumaron G-90® (Nittetsu Chemical Co., Ltd., Japan).

Resins having a polar group:

YS polystar T-115® and S-145® (Yasuhara Oil and Fat Co., Ltd., Japan), Steberite-ester 7® Hercules Inc.), and Neopolymer E-100® (Nippon Petrochemical Co., Ltd., Japan).

When the composition of the invention is used as the sealing material, optionally added is a plasticizer, a filler, a reinforcement, an antisagging agent, a colorant, an anti-aging agent, an adhesion promoting agent, a property modifier.

Specific examples of the plasticizer are phthalates (e.g. dibutyl phthalate, diheptyl phthalate, di(2-ethylhexyl) phthalate, butyl benzyl phthalate, butyl phthalyl glycolate); non-aromatic dibasic acid esters (e.g. dioctyl adipate, dioctyl sebacate), esters of polyalkylene glycol (e.g. diethylene glycol dibenzoate, triethylene glycol dibenzoate,); phosphates (e.g. tricresyl phosphate, tributyl phosphate,); chlorinated paraffines; hydrocarbon oils (e.g. alkylidiphenyl, partially hydrogenated terphenyl,) which are used alone or as a mixture thereof. The plasticizer may be added in the course of the polymerization.

Specific examples of the filler or reinforcement are heavy or light calcium carbonate, calcium carbonate having a surface treated with an aliphatic acid, a resin acid, a cationic surfactant, anionic surfactant and the like, magnesium carbonate, talc, titanium oxide, barium sulfate, alumina, metal powder (e.g. aluminum, zinc

and iron powder), bentonite, kaolin clay, fumed silica, silica powder, and carbon black. When a transparent filler or reinforcement such as fumed silica is used, a transparent sealing material is prepared.

Specific examples of the antisagging agent are hydrogenated castor oil, and metal soap such as calcium stearate, aluminum stearate and barium stearate. The anti-sagging agent may not be used depending on the end use and/or the presence of the filler or reinforcement.

As the colorant, conventional organic or inorganic pigment or dye may be used.

Specific examples of the property modifier are silane coupling agents such as alkylalkoxy silanes (e.g. methyltrimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane, n-propyltrimethoxysilane); alkylisopropenoxysilanes (e.g. dimethyldiisopropenoxysilane, methyltriisopropenoxysilane, γ -glycidoxypoly-
 10 methyldiisopropenoxysilane); alkoxy silane having a functional group (e.g. γ -glycidoxypoly-
 methylmethyldimethoxysilane, γ -glycidoxypolytrimethoxysilane, vinyltrimethoxysilane, vinyldimethyl-
 methoxysilane, γ -aminopropyltrimethoxysilane, N-(β -aminoethyl)aminopropylmethyldimethoxysilane, γ -mer-
 captopropyltrimethoxysilane, γ -mercaptopropylmethyldimethoxysilane); silicone varnish; polysiloxanes, etc.
 Addition of the property modifier can increase or decrease the hardness of the cured composition.

15 The adhesivity promoting agent is not necessarily added to the composition of the invention, since the polymer used according to the present invention itself has enough adhesivity to be applied on the surface of the various substrates such as glass, ceramics, metal, or the polymer can be adhered to various surfaces by the use of a primer. Specific examples of the adhesivity promoting agent are epoxy resins, phenol resins, silane coupling agents, alkyl titanate, aromatic polyisocyanate, and mixtures thereof.

20 The sealing material comprising the polymer composition of the invention may be formulated as a moisture curing one-pack type one by compounding all the components and stored in a sealed state. Alternatively, the sealing material may be formulated as a two-pack type one consisting of the polymer composition and a curing mixture containing the curing catalyst, the filler, the plasticizer, water and other suitable component(s) except the polymer, which are mixed in use.

25 In case of the one-pack type sealing material, since all the components are compounded beforehand, preferably, any component including water or moisture should be dehydrated before compounding, or the components are compounded with removing water or moisture, for example, under reduced pressure.

In case of the two-pack type one, since the polymer composition does not contain any curing catalyst, either the polymer composition and the curing mixture may contain a slight amount of water or moisture.
 30 However, for longer storage of the sealing material, it is advisable to dehydrate it. Solid components such as powder may be heated to dehydrate, and liquid components may be dehydrated under reduced pressure or with a desiccant such as synthetic zeolites, active alumina and silica gel. Alternatively or in addition, water or moisture can be removed by adding a small amount of isocyanate compound to react the isocyanate group with water or moisture. Furthermore, storage stability of the sealing material is improved
 35 by the addition of lower alcohol (e.g. methanol, ethanol,) or alkoxy silanes (e.g. n-propyltrimethoxysilane, vinylmethyldimethoxysilane, γ -mercaptopropylmethyldimethoxysilane, γ -glycidoxypolytrimethoxysilane,).

To improve processability of the polymer composition and/or to reduce the viscosity of the composition, a solvent may be used. Specific examples of the solvent are aromatic hydrocarbons (e.g. toluene, xylene,), esters (e.g. ethyl acetate, butyl acetate, amyl acetate, cellosolve acetate,), and ketones (e.g. methyl ethyl
 40 ketone, methyl isobutyl ketone, diisobutyl ketone,).

In addition to the pressure sensitive adhesive and the sealing material, the polymer composition of the invention may be used as an adhesive, a templating agent, an insulating material, a foaming material, a spraying material.

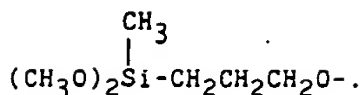
45 The present invention will be hereinafter explained further in detail by following examples, in which % and parts are by weight unless otherwise indicated.

Preparation Example 1

50 (Preparation of polyalkyleneoxide having silicon-containing reactive group)

In an autoclave equipped with a stirrer, polypropyleneoxide 98 % of the terminal groups of which being allylether groups (having average molecular weight, 8,000 and produced from polypropylene glycol) (800 g) and methyldimethoxysilane (20 g) were charged. Then, a solution of chloroplatinic acid (8.9 g of $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ dissolved in a mixture of 18 ml of isopropyl alcohol and 160 ml of tetrahydrofuran) (0.34 ml)
 55 was added, and the reaction was carried out at 80 ° C for 6 hours.

An amount of the unreacted silane was monitored by gaschromatography and infrared spectrum analysis to find that 84 % of the terminal groups were reacted and there were obtained polypropyleneoxide having a terminal group of the formula:



5

Preparation Example 2

10 (Preparation of acrylate polymer having silicon-containing reactive group)

To a mixture of n-butyl acrylate (128 g, 1.0 mole), γ -methacryloxypropylmethyldimethoxysilane (3.48 g, 0.015 mole) and γ -mercaptopropylmethyldimethoxysilane (2.46 g, 0.015 mole), α,α' -azobisisobutyronitrile (0.25 g) was added and dissolved. A part of the solution (30 g) was charged in a 300 ml four-necked flask equipped with a condenser and a dropping funnel the interior of which flask was replaced with nitrogen, and gradually heated on an oil bath kept at 70°C. Then, the exothermic polymerization was initiated and the viscosity of the solution increased. The residual solution was dropwise added over 2.5 hours. After the completion of the addition of the solution, the reaction mixture was stirred for 1 hour to complete the polymerization to obtain a colorless transparent viscous liquid. Viscosity (23°C), 35Pa.s (350 poise) Polymerization yield, 97 %.

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Preparation Example 3

25 (Preparation of acrylate polymer in the presence of polyalkyleneoxide)

Polypropyleneoxide (75 g) prepared in Preparation Example 1 was charged in a 300 ml four-necked flask the interior of which flask was replaced with nitrogen, and gradually heated with stirring on an oil bath kept at 110°C. From the dropping funnel, a mixture of n-butyl acrylate (25 g), γ -methacryloxypropylmethyldimethoxysilane (0.07 g) and α,α' -azobisisobutyronitrile (0.25 g) was added over 2 hours. After the completion of the addition of the mixture, the reactive mixture was stirred for 1 hour to obtain a colorless transparent viscous liquid. Viscosity (23°C), 54Pa.s (540 poise). Polymerization yield, 97.5 %.

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Examples 1-9

35 To the organic polymer having the silicon-containing reactive group prepared in each of the Preparation Examples (100 parts), a specific tackifier resin shown in Table 1 was added and then a toluene solution of them having a solid content of 80 % was prepared. To the solution, a curing catalyst shown in Table 1 was added and applied on a polyester substrate (Lumilar® film manufactured by Toray Co., Ltd., Japan) of 25 μ m in thickness with a coater to obtain a dried paste thickness of 25 μ m and cured at 110°C for 1 minute.

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In Table 1, "YS polystar T-115® and S-145"® are terpene-phenol resins manufactured by Yasuhara Oil and Fat Co., Ltd., Japan, and Steberite-ester 7® is a hydrogenated rosin ester resin manufactured by Hercules Inc.

45 Comparative Examples 1-5

In the same manner as in Example 1 but using a curing catalyst shown in Table 1, a solution was prepared and applied on the substrate.

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Curing property of the polymer composition was evaluated according to the following criteria:

A: The composition is substantially completely cured and the surface of the cured polymer is not sticky. When the cured polymer is adhered on a stainless steel plate and peeled off, the cured polymer does not remain on the plate.

B: Although the polymer is cured to a great extent, the surface of the cured polymer is very sticky. When the cured polymer is adhered on a stainless steel plate and peeled off, the cured polymer does not remain on the plate.

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C: The polymer composition is insufficiently cured so that when the cured polymer is adhered on a stainless steel plate and peeled off, a part of the polymer remains on the plate.

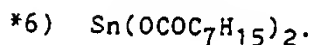
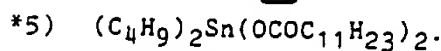
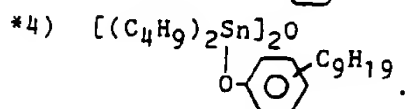
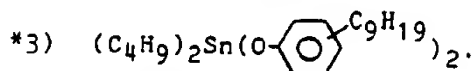
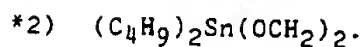
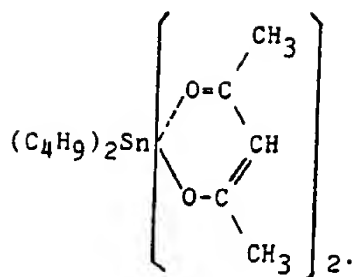
Table 1

Example No.	Polymer	Curing catalyst		Tackifier resin		Curing property
		Compound	Parts	Compound	Parts	
1	Prep. Ex. 1	Dibutyltin bisacetylacetonate *1)	3	YS polystar T-115	80	A
2	†	Dibutyltin dimethoxide *2)	3	†	†	A
3	†	Dibutyltin bisnonylphenoxide *3)	3	†	†	A
4	†	Dibutyltin monononylphenoxide *4)	3	†	†	A
5	†	Dibutyltin bisacetylacetonate	3	YS polystar S-115	80	A
6	†	†	3	Steberite-ester 7	80	B
7	†	†	1.5	YS polystar T-115	80	B
8	Prep. Ex. 2	†	3	†	40	A
9	Prep. Ex. 3	†	3	†	†	A

Table 1 (continued)

Comp. Example No.	Polymer	Curing catalyst		Tackifier resin		Curing property
		Compound	Parts	Compound	Parts	
1	Prep. Ex. 1	Dibutyltin dilaurate *5)	3	YS polystar T-1150	80	C
2	†	†	5	†	†	C
3	†	Tin dioctylate *6)	3	†	†	C
4	Prep. Ex. 2	Dibutyltin dilaurate	3	†	40	C
5	Prep. Ex. 3	†	†	†	†	C

Note *1)

Examples 10 and 11

To polyalkyleneoxide having the silicon-containing reactive group prepared in Preparation Example 1, calcium carbonate, dioctyl phthalate, titanium dioxide, hydrogenated castor oil and, as an anti-aging agent, Noclack NS-6® (manufactured by Ohuchi-Shinko Chemical Co., Ltd., Japan) in the predetermined amounts shown in Table 2 were added and mixed with removing water by azeotropic dehydration. Then, a curing catalyst was added with preventing contamination of water or moisture and again thoroughly mixed.

The curing time of the mixture, namely tack-free time defined in JIS (Japanese Industrial Standards) A-5758 was measured at $20 \pm 3^\circ\text{C}$. The curing time of the mixture after keeping it in a drier at 50°C for 1 month was also measured. The results are shown in Table 3.

Comparative Examples 6 and 7

In the same manner as in Example 11 but using dibutyltin dilaurate or tin dioctylate as the curing catalyst, the same procedures are repeated. The results are shown in Tables 2 and 3.

As is clear from Table 3, before keeping them in a dryer at 50°C for 1 month, it took longer time for curing the compositions of Comparative Examples 6 and 7 than those of the present invention. In addition, the curing time of the compositions of Comparative Examples after keeping in a dryer became undesirably long.

Table 2

	Example No.		Comp. Ex. No.	
	10	11	6	7
Polymer (Prep. Ex. 1)	100	100	100	100
Calcium carbonate	150	150	150	150
Diethyl phthalate	60	60	60	60
Titanium dioxide	30	30	30	30
Hydrogenated castor oil	4	4	4	4
Noclack NS-6 [®]	0.5	0.5	0.5	0.5
Dibutyltin diacetylacetonate	2	3	-	-
Dibutyltin dilaurate	-	-	3	-
Tin dioctylate	-	-	-	3

Table 3

		Example No.		Comp. Ex. No.	
		10	11	6	7
Tack free time (hrs)	Before keeping in a dryer	2.0	1.2	4.0	6.0
	After keeping in a dryer for 1 month at 50°C	2.0	1.2	8.0	>12.0

Examples 12 and 13

To polyalkyleneoxide having the silicon-containing reactive group prepared in Preparation Example 1, calcium carbonate, diethyl phthalate, titanium dioxide, hydrogenated castor oil and as an anti-aging agent, Noclack NS-6[®] in the predetermined amounts shown in Table 4 were added and mixed with removing water by azeotropic dehydration. Then, a curing catalyst and, as an adhesivity improving agent, A1120 (N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane manufactured by Nippon Unicar Co., Ltd., Japan) were added with preventing contamination of water or moisture and again thoroughly mixed.

The mixture was examined for tack-free time defined in Examples 10 and 11 on a substrate listed in Table 5 and then cured at 20°C for 7 days, followed by examination of adhesivity. The results are shown in Table 5.

Comparative Examples 8 and 9

In the same manner as in Example 12 but using dibutyltin dilaurate as the curing catalyst and laurylamine as a co-catalyst shown in Table 4, the same procedures are repeated. The results are shown in Table 5.

The composition containing dibutyltin dilaurate as the curing catalyst (Comparative Example 8) had high adhesive strength but a low curing rate. The composition containing a combination of dibutyltin dilaurate and laurylamine as the curing agent (Comparative Example 9) had a high curing rate but low adhesive strength.

Table 4

	Example No.		Comp. Ex. No.	
	12	13	8	9
Polymer (Prep. Ex. 1)	100	100	100	100
Calcium carbonate	100	100	100	100
Dioctyl phthalate	40	40	40	40
Titanium dioxide	25	25	25	25
Hydrogenated castor oil	4	4	4	4
Noclack NS-6 [®]	0.5	0.5	0.5	0.5
A1120	0.5	0.5	0.5	0.5
Dibutyltin monononylphenolate	2	-	-	-
Dibutyltin diacetylacetonate	-	2	-	-
Dibutyltin dilaurate	-	-	2	2
Laurylamine	-	-	-	1

Table 5

	Example No.		Comp. Ex. No.	
	12	13	8	9
Tack free time (hrs.)	0.5	0.4	4.0	0.8
<u>Adhesivity</u> *1)				
Glass	A	A	A	B
Anodized aluminum	A	A	A	B
Acryl baked aluminum	A	A	A	B
Aluminum colored by electrolysis	A	A	A	C
Polyvinyl chloride coated steel plate	A	A	A	C

Note *1) The composition was cured at 20°C for 7 days and the cured composition (the coated film on the substrate) was peeled off from the substrate with fingers. The adhesivity was evaluated based on the state of failure as follows:

A: Cohesive failure of the cured composition.

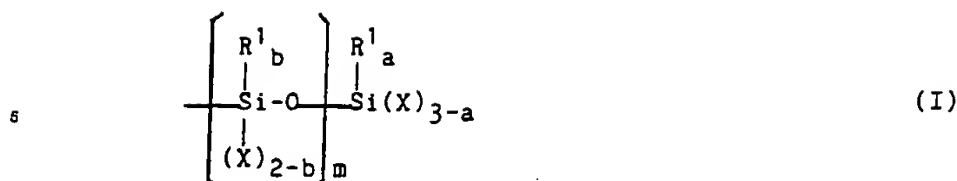
B: Cohesive failure of the cured composition on about a half of the surface area of the substrate.

C: Failure at the interface between the cured composition and the substrate.

Claims

1. A curable polymer composition comprising

(A) 100 parts by weight of an organic polymer comprising a backbone chain selected from polyalkyleneoxide with a molecular weight of 500 to 30,000, ether-ester block copolymer, vinyl polymer, vinyl type polymer with a molecular weight of 500 to 1,000,000 and diene type polymer and having at least one silicon-containing reactive group of the formula (I)

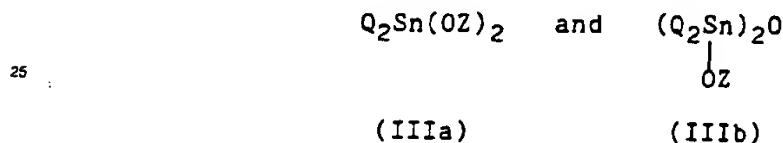


wherein R^1 is, the same or different, a C_1 - C_{20} monovalent hydrocarbon group or a triorganosiloxy group of the formula:



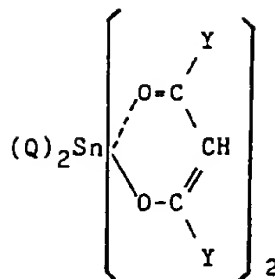
in which R' is, the same or different, a C_1 - C_{20} monovalent hydrocarbon group; X is a hydroxyl group or a hydrolyzable group provided that when the number of X s in the group (I) is at least 2, X s are the same or different; a is 0, 1, 2 or 3; b is 0, 1 or 2; and m is an integer of 1 to 18; wherein the silicon-containing reactive group (I) bonded to the backbone chain via a carbon atom directly attached to the silicon atom, and

(B) 0.01 to 10 parts by weight of a curing catalyst selected from the compounds of the formulas:



wherein Q is a C_1 - C_{20} monovalent hydrocarbon group; and Z is, the same or different, a C_1 - C_{20} monovalent hydrocarbon group or an organic group having a functional residue which can form a coordinate bond with Sn atom.

2. A curable polymer composition according to claim 1, wherein the organic polymer (A) has a backbone chain comprising alkyleneoxide polymer which consists of repeating units of the formula:
 $-R^4-O-$
 wherein R^4 is a C_1 - C_8 , preferably C_1 - C_4 divalent hydrocarbon group.
3. A curable polymer composition according to claim 2, wherein the alkyleneoxide polymer has a molecular weight of 3,000 to 15,000.
4. A curable polymer composition according to claim 3, wherein the alkyleneoxide polymer has the silicon-containing reactive group at the chain end of molecule.
5. A curable polymer composition according to claim 1, wherein the organic polymer (A) has a backbone chain comprising polyalkyl acrylate having 2 to 12 carbon atoms in the alkyl group.
6. A curable polymer composition according to claim 1, wherein the curing catalyst is a compound of the formula:

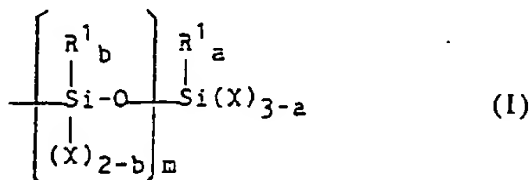


wherein Q is, the same or different, a C₁-C₂₀ monovalent hydrocarbon group; and Y is, the same or different, a C₁-C₈ hydrocarbon group, halogenated hydrocarbon group, cyanoalkyl group, alkoxy group, halogenated alkoxy group, cyanoalkoxy group or amino group.

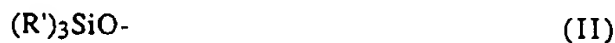
Revendications

1. Composition de polymère durcissable, comprenant:

(A) 100 parties en poids d'un polymère organique comprenant un squelette choisie parmi un poly-(oxyde d'alkylène) ayant une masse moléculaire de 500 à 30.000, un copolymère séquencé éther-ester, un polymère vinylique, un polymère du type vinyle ayant une masse moléculaire de 500 à 1.000.000 et un polymère du type diène, et ayant au moins un groupe réactif contenant du silicium, de formule (I):



où R¹ peut être identique ou différent et représente un groupe hydrocarbure monovalent en C₁-C₂₀ ou un groupe triorganosiloxy de formule :



où R' peut être identique ou différent et représente un groupe hydrocarbure monovalent en C₁-C₂₀ ; X est un groupe hydroxyle ou un groupe hydrolysable, étant entendu que lorsque le nombre des X dans le groupe (I) est au moins 2, les X sont identiques ou différents a est 0, 1, 2 ou 3; b est 0, 1 ou 2; et m est un nombre entier de 1 à 18 où le groupe réactif (I) contenant du silicium est lié au squelette par l'intermédiaire d'un atome de carbone lié directement à l'atome de silicium, et

(B) 0,01 à 10 parties en poids d'un catalyseur de durcissement choisi parmi les composés répondant aux formules :



où Q est un groupe hydrocarbure monovalent en C_1-C_{20} ; et Z, qui peut être identique ou différent, est un groupe hydrocarbure monovalent en C_1-C_{20} ou un groupe organique ayant un résidu fonctionnel qui peut former une liaison de coordination avec l'atome de Sn.

2. Composition de polymère durcissable selon la revendication 1, dans laquelle le polymère organique (A) a un squelette comprenant un polymère d'oxyde d'alkylène, qui est constituée par des motifs répétitifs de formule :



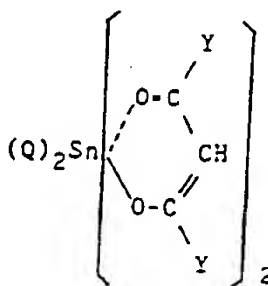
où R^4 est un groupe hydrocarbure bivalent en C_1-C_8 , de préférence en C_1-C_4 .

3. Composition de polymère durcissable selon la revendication 2, dans laquelle le polymère d'oxyde d'alkylène a une masse moléculaire de 3.000 à 15.000.

4. Composition de polymère durcissable selon la revendication 3, dans laquelle le groupe réactif contenant le silicium est à l'extrémité de la chaîne moléculaire du polymère d'oxyde d'alkylène.

5. Composition de polymère durcissable selon la revendication 1, dans laquelle le polymère organique (A) a un squelette comprenant un poly(acrylate d'alkyle) dont le groupe alkyle comprend 2 à 12 atomes de carbone.

6. Composition de polymère durcissable selon la revendication 1, dans laquelle le catalyseur de durcissement est un composé de formule :



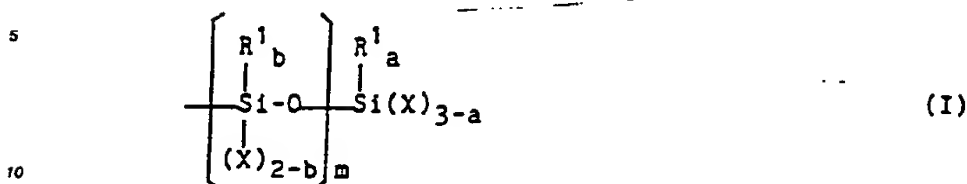
où Q peut être identique ou différent et représente un groupe hydrocarbure monovalent en C_1-C_{20} et Y, qui peut être identique ou différent, représente un groupe hydrocarbure en C_1-C_8 , un groupe hydrocarbure halogéné, un groupe cyanoalkyle, un groupe alcoxy, un groupe alcoxy halogéné, un groupe cyanoalcoxy ou un groupe amino.

Ansprüche

1. Vulkanisierbare Polymerzusammensetzung, enthaltend

(A) 100 Gewichtsteile eines organischen Polymers, enthaltend eine Kammkette, ausgewählt aus einem Polyalkylenoxid mit einem Molekulargewicht von 500 bis 30.000, einem Etheresterblockcopolymer, einbtem Vinylpolymer, Polymer vom Vinyltyp mit einem Molekulargewicht von 500 bis 1.000.000

und einem Polymer vom Dientyp; und mindestens einer Siliziumhaltigen reaktiven Gruppe der Formel (I)

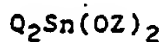


worin R' die gleiche oder eine verschiedene C₁ bis C₂₀ monovalente Kohlenwasserstoffgruppe oder eine Triorganosiloxygruppe der Formel (II) ist,

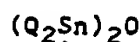
(R')₃ SiO-

bei der R' die gleiche oder eine verschiedene C₁ bis C₂₀ monovalente Kohlenwasserstoffgruppe ist; X ist eine Hydroxylgruppe oder eine hydrolysierbare Gruppe mit der Bedingung, daß wenn die Anzahl der X in der Gruppe (I) wenigstens 2 ist, sind die X gleich oder verschieden; a ist 0, 1, 2 oder 3, b ist 0, 1 oder 2; und m ist eine ganze Zahl von 1 bis 18; wobei die siliziumhaltige reaktive Gruppe (I) an die Stammkette über ein Kohlenstoffatom, das direkt am Siliziumatom sitzt, gebunden ist, und

(B) 0,01 bis 10 Gewichtsteile eines Vulkanisationskatalysators, ausgewählt aus den Verbindungen der Formeln (IIIa) und (IIIb)



(IIIa)



(IIIb)

worin Q eine C₁ bis C₂₀ monovalente Kohlenwasserstoffgruppe ist und Z ist dieselbe oder eine verschiedene C₁ bis C₂₀ monovalente Kohlenwasserstoffgruppe oder eine organische Gruppe mit einem funktionalen Rest, der eine Koordinationsbindung mit einem Zinnatom ausbilden kann.

2. Vulkanisierbare Polymerzusammensetzung nach Anspruch 1, worin das organische Polymer (A) eine Stammkette hat, enthaltend ein Alkylenoxidpolymer bestehend aus sich wiederholenden Einheiten der Formel

-R'-O-

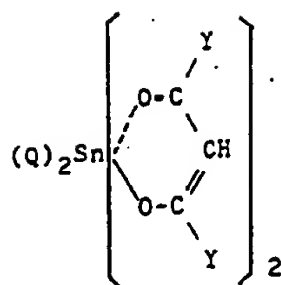
worin R' eine C₁ bis C₈, vorzugsweise eine C₁ bis C₄ divalente Kohlenwasserstoffgruppe ist.

3. Vulkanisierbare Polymerzusammensetzung nach Anspruch 2, worin das Alkylenoxidpolymer ein Molekulargewicht von 3.000 bis 15.000 hat.

4. Vulkanisierbare Polymerzusammensetzung nach Anspruch 3, worin das Alkylenoxidpolymer eine siliziumhaltige reaktive Gruppe am Kettenende des Moleküls hat.

5. Vulkanisierbare Polymerzusammensetzung nach Anspruch 1, worin das organische Polymer (A) eine Stammkette hat, enthaltend ein polyalkylacrylat mit 2 bis 12 Kohlenstoffatomen in der Alkylgruppe.

6. Vulkanisierbare polymerzusammensetzung nach Anspruch 1, worin der Vulkanisationskatalysator eine Verbindung der Formel



ist, worin Q die gleiche oder eine verschiedene C₁ bis C₂₀ monovalente Kohlenwasserstoffgruppe ist, und Y ist die gleiche oder eine verschiedene C₁ bis C₈ Kohlenwasserstoffgruppe, halogenierte Kohlenwasserstoffgruppe, Cyanoalkylgruppe, Alkoxygruppe, halogenierte Alkoxygruppe, Cyanoalkoxygruppe oder eine Aminogruppe.

